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Methane production from lignocellulosic agricultural crop wastes: A review in context to second generation of biofuel production

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ABSTRACT

The aim of this paper is to present a comprehensive review on renewable methane fuel production through the biological route of biomethanation process from major lignocellulosic agricultural crop waste biomass (maize, wheat, rice and sugarcane). Global annual approximate production of major agriculture based lignocellulosic biomass has been explored. Fundamental requirements of biomethanation process have been discussed in details for optimum production of methane. The essential properties of biomass (proximate, ultimate and compositional) conscientious for quality of derived fuel have also been presented along with the pretreatment requirements for lignocellulosic biomass. Methane generation potential of the major lignocellulosic agricultural crop biomass has been explored and presented. Furthermore, the methane production potential and its energetic analysis have also been compared with the bio-ethanol productions. The overall parametric analysis involved in anaerobic digestion and alcoholic fermentation explore that methane generation from lignocellulosic agricultural crop waste biomass is more economical and environmentally beneficial way of biomass utilization in a sustainable way of energy production.

Contents

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Nomenclature

BMP	biochemical methane potential
C	carbon
C/N	carbon–nitrogen ratio
$Ca(OH)_2$	calcium hydroxide
CH_4	methane
CO	carbon monoxide
CO_2	carbon dioxide
COD	chemical oxygen demand
d	day
DM	dry matter
EJ	Exa joule
g	gram
H_2	hydrogen
H_2O	water
ha	hectare
HC	hydrocarbons
IPCC	intergovernmental panel on climate change
kg	kilo gram
km	kilo metre
KOH	potassium hydroxide
L	litre
m^3	cubic metre
$Mg(OH)_2$	magnesium hydroxide
MJ	mega joule
mm	milli metre
MSW	municipal solid wastes
mV	milli volts
NaOH	sodium hydroxide
NO_x	nitrogen oxides
°C	degree Celsius
OLR	organic loading rate
PM	particulate matter
SO_2	sulphur dioxide
TS_a	total solids added
VS	volatile solids
VS_a	volatile solids added

1. Introduction

In the 20th century, major research emphasis have been the centre of development of fossil crude oil, coal and natural gas based refinery to exploit the cheaply available fossil feedstock for development of industry to produce multiple products and energy to meet the growing demand of the population [1,2]. In the 21st century, fossil fuel resources are not regarded as sustainable in ecological and environmental point of views. Currently, 90% of the energy carriers used is of fossil origin and their use is associated with the emission of carbon dioxide to the atmosphere. Every year our earth's atmosphere receives more than 15 billion tonnes of CO_2. The combustion of fossil fuels is a big contributor to increase the level of CO_2 in the atmosphere which is directly associated with global warming [3,4]. The adverse effects of greenhouse gas emissions on the environment, together with declining petroleum reserves and future energy security have been realized in well. Therefore, there is renewed interest in the production and use of fuels originated from plants or organic wastes for sustainable development of economy and society in an eco-friendly manner. Biomass resources are the only suitable and renewable primary energy resource that can provide alternative transportation fuels in the short-term [5,6].

One of the major drivers for worldwide biofuels development is the concern about global climate change that is primarily caused by burning of fossil fuels. There is substantial scientific evidence that the accelerating global warming is a cause of greenhouse gas emissions. One of the main greenhouse gases in carbon dioxide. However, nitrous oxide, methane and several other compounds are greenhouse gases, which are even more severe to global warming than carbon dioxide [7].

The second generation of biofuel production mainly focuses on the production of biofuels from the renewable resources, which could help to minimize the fossil fuel combustion and CO_2 production in concern to help in preventing the global warming of the our planet "Earth". Biofuels produced from biomass such as plants or organic waste could help to reduce both the world's dependence on oil and CO_2 production. These biofuels have the potential to cut CO_2 emission because the plants are made with the use CO_2 as they grow [8]. Thus, the utilization of biomass resources will be one of the most important factors for environmental protection in the 21st century. Biofuels and bio-products produced from plant biomass would mitigate global warming. Biomass absorbs CO_2 during growth and emits it during combustion. Therefore, biomass helps the atmospheric CO_2 recycling and does not contribute to the greenhouse effect. Biomass production consumes the same amount of CO_2 from the atmosphere during growth as is released during combustion. Simultaneously, biofuel production along with bio-products can provide new income and employment opportunities in rural areas [9,10]. In an eco-friendly development of human being and for the abatement of greenhouse gases emission, it is recommended to have more efficient alternatives based on renewable and conventional technologies [11].

The second generation of biofuels production from renewable resources 'plant biomass' refers particularly to the lignocellulosic biomass/materials, as this makes up the majority of the cheap and abundant non-food materials available from the plants. Therefore, lignocellulosic feedstock can offer the potential to provide novel biofuels of the "second generation of biofuels" [12]. The production of hydrogen, natural gas, bio-oils, producer gas, biogas, alcohols and biodiesel from renewable biomass have been the major research centre around the world with a

Table 1
Comparison of gaseous emissions from some fuels used in heavy vehicles (in bus).

g/km	CO	HC	NO_x	CO_2	PM
Diesel	0.20	0.40	9.73	1053	0.100
Natural gas	0.40	0.60	1.10	524	0.022
Biogas	0.08	0.35	5.44	223	0.015

A report on biogas technology and biogas use in Sweden, Traffic and Public Transport Authority, City of Gothenburg, November 2000.

view to supplement petroleum fuels and reduce environmental pollution.

Methane production from a variety of biological wastes through anaerobic digestion technology is growing worldwide and is considered ideal in many ways because of its economic and environmental benefits. Furthermore, the other crucial benefits offered by the use of biogas over natural gas are as; (i) it is produced from renewable resources, (ii) it does not add any greenhouse gases in the atmosphere, (iii) it is produced locally without any dependency on foreign oil or natural gas supplies, (iv) it helps in reducing the pollution produced by the organic wastes, which account for most fresh water pollution, and, (v) it helps in retarding the waste management problems. Methane fermentation technology is a most efficient way of handling and energy generation from biomass, in term of energy output/input ratio (28.8 MJ/MJ) in comparison to all other technology of energy production through biological and thermo-chemical routes of energy conversion processes [13]. According to the IPCC 2001, the global warming potential of methane over 100 years relative to the carbon dioxide is 23 times higher [7]. Therefore, it is essential to reduce natural emission of methane that naturally occurs due to self-decomposition of biomass left outside (particularly wet and highly perishable containing high moisture). The biomass containing high moisture content when left in the environment in form of a heap, then the upper biomass that is directly in contact of open atmosphere is subjected to aerobic degradation. However, the inner biomass that is not in contact with oxygen undergoes through anaerobic digestion and releases methane into the open atmosphere. This again leads the global warming in a substantial amount.

Furthermore, biogas after methane enrichment is as good as natural gas for powering the internal combustion engines used for various power generations and automobiles. Thus, biogas is a good substitute of the conventional compressed natural gas which is derived from crude petroleum. Along with, the biogas production from plant biomass being as CO_2 neutral, its combustion again lowers the emissions in comparison to gasoline, diesel fuel and even in natural gas as shown in Table 1 [14].

Keeping aforesaid statements into the considerations, this paper aimed to present one-sight comprehensive information on production and potential of major lignocellulosic agricultural crop derived waste biomass for methane generation via anaerobic digestion route of energy conversion process. Informative details on annual production of agricultural crop wastes biomass, fundamental requirements for methane generation, properties of lignocellulosic biomass and pretreatment methods for effective conversion into energy, methane generation potential and a comparative view with respect to bio-ethanol production potential have been presented.

2. Biomass resources and biomass from agriculture

2.1. Biomass resources

Biomass has the largest potential and can only be considered as the best option for meeting the demand and insurance of future energy/fuel supply in a sustainable manner. The modernization of biomass technologies leading to more efficient biomass production and conversion is one possible direction for efficient utilization of biomass resources. The main biomass processes utilized in the future are expected to be the direct combustion of residues and wastes for electricity generation, ethanol, biogas and biodiesel as liquid fuels, and combined heat and power production from energy crops. The future of biomass electricity generation lies in biomass integrated gasification/gas turbine technology, which offers high energy conversion efficiencies. Bio-energy currently contributes 10–15% (approximately 45 EJ) of total world energy use and several countries have established targets for the use of fuels produced from biomass. Numerous scenario studies suggest that the potential market shares of modern biomass utilization till the year 2050 would be of about 10–50% [10].

The annual global primary production of biomass is about 220 billion tonnes on dry weight basis that is equivalent to 4500 EJ of solar energy captured each year. From this biomass, an annual bioenergy market of 270 EJ could be possible on a sustainable basis [15]. Biomass is considered an attractive alternative to fossil fuels as a source of energy but only if it can be produced and utilized without adversely affecting the environment [16]. The most important biomass energy sources are wood and wood wastes, agricultural crops and their waste by-products, MSW, animal wastes, wastes from food processing, and aquatic plants and algae [17]. The average majority of biomass energy is produced from wood and wood wastes (64%), followed by MSW (24%), agricultural waste (5%), and landfill gases (5%) [18–21]. The amount of the wood waste resource depends upon how much wood is harvested for lumber, pulp and paper. Fuel-wood can be grown in plantations like a crop. Fast growing species such as poplar, willow or eucalyptus can be harvested after every few years. It is possible to harvest 10–13 tonnes of dry matter biomass per hectare per annum, with short-rotation poplar coppices grown in three 7-year rotations on soil of average or good quality [22]. Waste wood from the forest products industry such as bark, sawdust, board ends etc. are widely used for energy production. Presently, this industry in many cases is a net exporter of electricity generated by the combustion of wastes.

2.2. Biomass from agriculture

Agriculture and forestry are the only two sources of renewable carbon. Agriculture has the potential to help in meeting the growing energy and raw material demands of a society in a sustainable manner, as part of the vision towards a bio-based economy. These include the lowering greenhouse gas emissions and bringing benefits to soil and water quality along with the ecological biodiversity. Further, the agricultural biomass can only be considered sustainable if it is economically efficient and profitable, socially viable, provide a net benefit in improving the environmental performance and rural development, and is compatible with policy goals for agriculture, environment, energy, industry, and in the wider context of trade liberalization and sustainability [23].

Agricultural biomass is a relatively broad category of biomass that includes the food based portion (oil and simple carbohydrates) of crops (such as corn, sugarcane, beets) and the non-food based portion (complex carbohydrates) of crops (such as the leaves, stalks, and cobs of corn stover, orchard trimmings, rice husk, straw), perennial grasses, and animal waste. Generally, a range of biomass resources obtained from agriculture and forestry can be classified into five categories based on their physical characteristics as described in Table 2. Large quantity of crops residues are produced annually worldwide and often dumped in open environment. These include cereal crops straw, rice husk, bagasse, maize cobs, coconut husk, groundnut and other nutshells and sawdust [25]. The dumping of biomass in open environment is not a

Table 2
Category of biomass resources [24].

Sl. no.	Feedstock type	Definitions	Resources
1	Sugars/starches	Traditional agricultural crops suitable for fermentation using first generation technologies, some food processing residues are sugar and starch materials	Agricultural crops (sugars/starches), food processing residues containing residual sugars
2	Lignocellulosic biomass	Clean woody and herbaceous materials from a variety of sources includes clean urban biomass that is generally collected separately from the municipal waste stream (wood from the urban forest, yard waste, used pallets)	Agricultural residues, cellulosic energy crops, food processing residues, forest residues, mill residues, urban wood wastes, yard wastes
3	Bio-oils	Traditional edible and non-edible oil crops and waste oils suitable for conversion to bio-diesel	Agricultural and forestry oil bearing crops and trees, waste oils/fats/grease
4	Solid wastes	Primarily lignocellulosic biomass, but that may be contaminated (e.g., construction and demolition woods) or co-mingled with other biomass types	Municipal solid waste, construction and demolition wood, food wastes, non-recycled paper, recycled materials
5	Other wastes	Other biomass wastes that are generally separate from the solid waste stream which include biogas and landfill gas	Animal waste, waste from wastewater treatment biogas and landfill gas

recommendable practice in term of environmental and ecological aspects of sustainable development.

Top four major agricultural crops grown in the world are maize, wheat, rice, and sugarcane, respectively in term of total cultivated area and production. Thus, these four crops produces majority of lignocellulosic biomass in agriculture sector. Table 3 presents the world total cultivated area and production yield of major agricultural crops. According to the data of the Food and Agriculture Organization of the United Nations, 1.9% of total global rice production is from Japan in 2009–2010, which amounted to 9.74 million tonnes [27]. Furthermore, the total global sugarcane production in year 2007 stood at 1.59 billion metric tonnes with an average productivity of about 67.0 metric tonnes/ha. Major sugarcane producing countries are India, Brazil, Philippine, China, USA, Mexico, Indonesia, Australia and Colombia. Brazil and India produces almost 60% of all the sugarcane in the world, with Brazil producing about 35% of the global total [28]. Dry biomass production yield of sugarcane crop widely varies from 0.47 to 20.28 tonnes/ha in-plant crop and 4.57–60.10 tonnes/ha in-ratoon crop. Thus, on average sugarcane crop annually produces an approximate dry biomass yield of 40.0 tonnes/ha [29]. The analysis of data given in Table 3, provide an outlook estimate of the annual biomass production yield from only major agricultural crops and is presented in Table 4.

The above estimate of annual biomass production from maize, wheat, rice and sugarcane crops yields about 5358.54 million tonnes of dry biomass. Though, its major part is utilized as feed for animals, but a huge amount of this biomass remains unutilized and or is burnt in field open environment. Rice husk and sugarcane bagasse are usually accumulated in large volumes at one site. Rice husk is among the commonest agricultural residue. Rice husk amounts 20–25% of the harvested rice grain on dry weight basis, which is usually separated from rice grain at the processing centres [25].

An emission estimate of direct combustion of biomass yields into emission of 1599 kg carbon dioxide, 111.3 kg carbon monoxide, 9.2 kg methane, 5.6 kg hydrocarbon and 4.8 kg particulate matter per tonne of dry biomass [33]. Though, the direct burning of biomass in open environment theoretically does not produce carbon dioxide, as biomass is carbon neutral and does not contribute to the greenhouse effect. However, it is not a recommendable practice for sustainable development. Therefore, this biomass must be utilized properly and effectively for production of fuels/chemicals. This certainly helps in lowering down the overall global warming potential from other greenhouse gases, since environmental protection along with the energy generation is of a great concern in the 21st century.

3. The biomethanation process and its basic requirements

3.1. The biomethanation process

The biomethanation (methane fermentation) is a complex biological process, which can be divided in four phases of biomass degradation and conversion, namely hydrolysis, acidogenesis, acetogenesis, and methanation. The individual phases are carried out by different groups of micro-organisms (bacteria), which partly stand in syntrophic interrelation and place different requirements, on the environment [13]. Fig. 1a and b shows all the four complete stages of biomethanation process and percentage conversion of COD available in volatile part of biomass. All four stages of biomethanation process are discussed below.

3.1.1. Hydrolysis phase

Undissolved compounds like cellulose (a form of carbohydrates), proteins, and fats are cracked down into monomers (water-soluble fragments) by exoenzymes (hydrolase) of facultative and obligatorily anaerobic bacteria. Actually, in this phase the covalent bonds are split in a chemical reaction with water. The hydrolysis of carbohydrates takes place within a few hours, while hydrolysis of proteins and lipids may take a few days. The degradation of lignocellulose and lignin is slow and incomplete [13]. The facultative anaerobic micro-organisms take the oxygen dissolved in the water and thus cause the low redox potential necessary for obligatorily anaerobic micro-organisms. The conversion of carbohydrates into simple sugars, lipids (fats) into fatty acids and proteins into amino acids take place in the hydrolysis phase [34].

3.1.2. Acidogenic phase

The monomers formed in the hydrolytic phase are taken up by different facultative and obligatorily anaerobic bacteria and are degraded into short-chain organic acids, C_1–C_5 molecules (e.g. butyric acid, propionic acid, acetate, and acetic acid), alcohols, hydrogen, and carbon dioxide. The concentration of the intermediately formed hydrogen ions affects the kind of the products of the fermentation. The higher the partial pressure of hydrogen, the fewer reduced compounds (like acetate) are formed. Overall, during this phase simple sugars, fatty acids and amino acids are converted into organic acids, and alcohols [34].

3.1.3. Acetogenic phase

The products from the acidogenic phase serve as substrate for other bacteria, in the third phase. In the acetogenic phase, homoacetogenic micro-organisms constantly reduce exergonic H_2 and CO_2 to acetic acid. Acetogenic bacteria grow in a symbiotic

Table 3
World total maize, wheat and rice production in 2009 [26].

Sl. no.	Crop	Total cultivated area, million ha	Total grain yield, million tonnes	Major producing countries
1	Maize	159.531	817.110 (5.12)	USA, China, Brazil, India, Mexico, Argentina
2	Wheat	225.437	681.915 (3.02)	China, India, Russia, USA, Australia, France
3	Rice	161.420	678.688 (4.20)	India, China, Indonesia, Bangladesh, Thailand, Viet Nam, Japan

Figures in parenthesis () shows the world average grain productivity in tonnes/ha.

Table 4
Estimated world annual production of major agricultural crop based biomass.

Sl. no.	Crop	Average grain-to-aerial biomass ratio	Total estimated dry biomass production, million tonnes
1	Maize	0.30 [30]	2723.70
2	Wheat	1.0 [31]	681.92
3	Rice	0.75 [32]	904.92
4	Sugarcane	40 tonnes dry biomass/ha [29]	1048.00 (from 26.2 million hectare crop area)

relationship with methane-forming bacteria. During this phase, organic acids and alcohols are converted into acetate. Acetate serves as a substrate for methane-forming bacteria. For example, when ethanol (CH_3CH_2OH) is converted to acetate, carbon dioxide is used and acetate and hydrogen are produced. If the hydrogen accumulates and significant hydrogen pressure occurs, then the termination of activity of acetate-forming bacteria comes into play and the lost of acetate production occurs. However, methane-forming bacteria utilize hydrogen in the production of methane and significant hydrogen pressure does not occur.

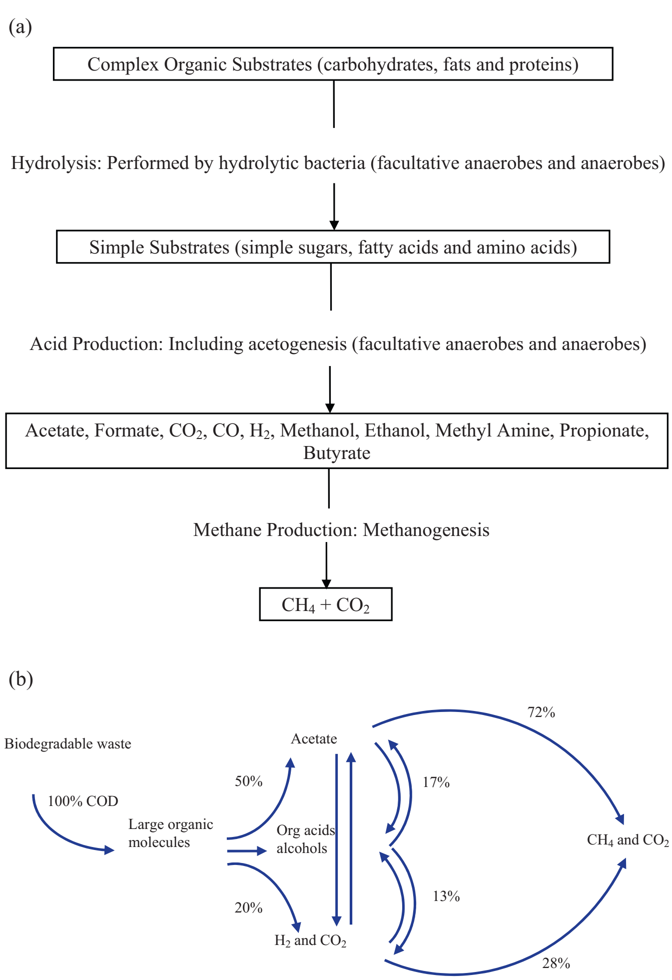


Fig. 1. a. Processwise stages of biomethanation process. b. Conversion of COD available in biomass in pathway of methane fermentation.
Redrawn from Ref. [35].

3.1.4. Methanogenic phase

In this phase, the methane formation takes place under strict anaerobic condition. This reaction is categorically exergonic. As follows from the description of the methanogenic micro-organisms, not all methanogenic species degrade all substrates. One can divide substrates acceptable for methanogenesis into the following three groups:

(I) Acetoclastic methanogenesis		
Acetate	→	$CH_4 + CO_2$
(II) Hydogenotrophic methanogenesis		
$H_2 + CO_2$	→	CH_4
(III) Methyltrophic methanogenesis		
Methanol	→	$CH_4 + H_2O$

Two biochemical components that seems unique to methanogens, is that they have mechanism of hydrogen oxidation and carbon dioxide reduction. Methanogenic bacteria utilize H_2 with CO_2, formate, methanol, and acetate as substrates for methanogenesis [36]. The methanogenic bacteria use carbon dioxide as the terminal electron acceptor and produces methane [37]. Table 5 shows the optimal environmental requirements for efficient play of bacteria involved in different stages of biomethanation process.

3.2. Basic parametric requirements

There are some basic requirements for effective play of anaerobic bacteria (hydrolytic, acidogenetic, acetogentic and methanogenetic) those degrade the particular biomass in terms of feed compositions and environmental conditions inside the reactor. These basic requirements for efficient operation of biomethanation system are as follows.

3.2.1. Retention time

Generally higher retention time yields higher cumulative biogas yield and results higher total volatile solid mass reduction. Rate of gas generation is initially high and then gradually declines as the digestion approaches towards completion [38–40]. High retention time value maximize volatile mass removal capacity, increases required digester volume, and provide buffering capacity for protection against the effects of shock loadings and toxic compounds in wastewaters and sludge of the reactor. High retention time values also help to permit biological acclimation to toxic compounds [34].

The conversion of volatile solids into gaseous products in an anaerobic digester is controlled by the retention time. The design of the retention time is a function of the final disposition of the

Table 5
Optimal environmental requirements for biomethanation process [13].

Parameter	Hydrolysis/Acidogenesis	Methane formation
Temperature	25–35 °C	Mesophilic: 32–42 °C thermophilic: 50–58 °C
pH value	5.2–6.3	6.7–7.5
C:N ratio	10:1–45:1	20:1–30:1
DM content	<40% DM	<30% DM
Redox potential	+400 to −300 mV	<−250 mV

digested sludge. The retention time may be relatively high or low, if the digested sludge is to be land applied or incinerated, respectively. However, increase in retention time >12 days do not contribute significantly to increase the destruction of volatile solids. Retention time values affect the rate and extent of methane production. Retention time is perhaps the most important operational condition affecting the conversion of volatile solids into gaseous products [34].

Methanogenic micro-organisms have a long regeneration time in general. To avoid washing out from the reactor, hydraulic residence times must be at least 10–15 days with reactor systems, which do not have facilities for retaining and returning biomass. In comparison with this, the regeneration time of hydrolytic and acid forming bacteria is significantly shorter, in order to avoid the risk of their washout. The low growth rate of methanogenics means that the biogas plant has a relatively long start-up phase i.e. up to 3 months. This is because of the reason that the amount of required inoculating sludge necessary to start the plant at its full capacity, is mostly not available immediately after feeding [13]. On other hand side, the reduction in retention time considerably, helps in reduction of the cost of biogas plant due to reduction in digester volume, without compromising on quantity and quality of biogas.

3.2.2. Process temperature

The variations in operating temperature of digester even a few degrees affect almost all the biological activity including the inhibition of some anaerobic bacteria, especially methane-forming bacteria. Adequate mixing of the digester content prevents the development of localized pockets of temperature variation. Most methane-forming bacteria are active in two temperature ranges. These ranges are the mesophilic range 30–35 °C and the thermophilic range 50–60 °C. At temperatures between 40 and 50 °C, methane-forming bacteria are inhibited [13].

Anaerobes are most active in the mesophilic and thermophilic temperature range [38]. The length of fermentation period is dependent on temperature. Digester performance falters somewhere near to 42 °C that represents the transition from mesophilic to thermophilic organisms [34]. Fig. 2 depicts the operating temperature of mesophilic and thermophilic methane-forming bacteria in relation to retention time of the biomethanation process. Methane-forming bacteria are active and grow in several temperature ranges. However, most of the methanogenic micro-organisms belong to the mesophilic and only a few are thermophilic. Further, the methanogens are very sensitive to sudden thermal changes. Therefore, any drastic change in operating temperature should be avoided. Anaerobic digestion in the psychrophilic temperature range (10–20 °C) is usually confined to small-scale treatment units such as Imhoff tanks, septic tanks, and sludge lagoons. In this the digestion process is not heated and the temperature of the digester sludge is approximately equal to the outside environment. Therefore, the rate of digestion of sludge varies from season to season.

The psychrophilic, mesophilic and thermophilic methanogens convert the organic substrates into methane [38]. The psychrophilic produces methane when the process temperature is up to 20 °C and converts a lesser quantity of biodegradable volatile solids, thus producing a very low amount of biogas [41]. Mesophilic come into play in the temperature range of 20–45 °C and the biogas production reaches the maximum when the process temperature is maintained around 35 °C [42]. Thermophilic operation provides benefits of short degradation time, good reduction of pathogens, high gas production and good sludge separation. But it is more difficult to control the process.

3.2.3. pH

In biomethanation process, pH significantly affects its performance and is an important parameter affecting the growth of a variety of micro-organisms involved in various stages during operation of the process [38,40]. The pH of the digester can be kept within a desired range by feeding an optimal organic loading rate. A pH outside the range of 6.0–8.5 starts showing toxic effect on methanogens population. The pH of the system depends on the rate at which intermediates are formed during fermentation. The drop in pH below 6.6 adversely affects the activities of the methanogens while a pH of 6.2 becomes toxic. The acid production is continuing even at this pH because the acidogenic bacteria produces acid until the pH drops to 4.5–5.0 [43].

The acceptable enzymatic activity of acid-forming bacteria occurs above pH 5.0, but acceptable enzymatic activity of methane-forming bacteria does not occur below pH 6.2. Most anaerobic bacteria, including methane-forming bacteria perform well within a pH range of 6.8–7.2. The pH in an anaerobic digester initially decreases below 6.0 with the production of volatile acids and as a great deal of carbon dioxide is given off. After this, the pH rises above neutral i.e. 7.0–8.0 and more. However, as methane-forming bacteria consume the volatile acids and alkalinity is produced due to more methane and carbon dioxide production, the pH of the digester increases and then stabilizes [34,44]. At hydraulic retention times >5 days, the methane-forming bacteria begins to rapidly consume the volatile acids. In a properly operating anaerobic digester, a pH in between 6.8 and 7.2 occurs as volatile acids are converted to methane and carbon dioxide. The pH of an anaerobic system is significantly affected by the carbon dioxide content of the biogas [34]. The percentage of CO_2 in biogas increases with

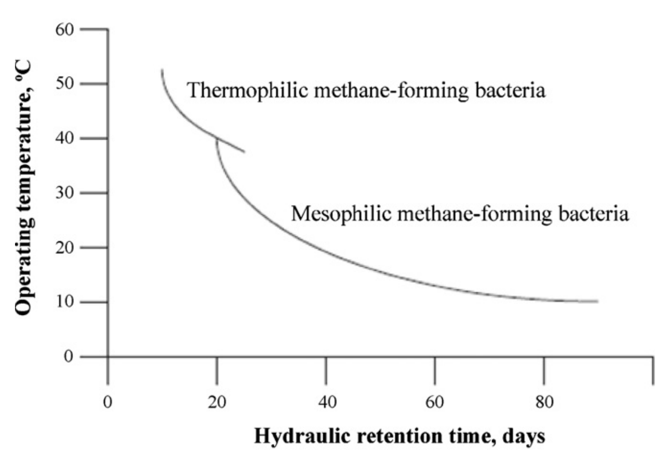


Fig. 2. Operating temperature of methanogenic bacteria in relation to digestion time [34].

decreasing pH values and with excessive activity of the hydrolytic and acetogenic micro-organisms since CO_2 cannot be completely used by methanogenic bacteria [45]. The optimum range of pH for methane production is 7.0–7.2, although gas production may occur satisfactorily between pH 6.6 and 7.6. However, drop in pH below 6.6 could cause significant inhibition and acidic condition of pH 6.2 is toxic to methanogens [46].

The optimum pH for the methane-forming micro-organism is at pH 6.7–7.5. Therefore, it is important to adjust the pH value in the second stage higher than that in the first stage of a two stage biogas plant. Only *Methanosarcina* is able to withstand lower pH values (6.5 and below). With the other bacteria, the metabolism is considerably suppressed at pH < 6.7. If the pH value sinks below 6.5, then the production of organic acids leads to a further decrease of the pH value by the hydrolytic bacteria and possibly to cessation of the fermentation. In the reality, the pH value is held within the neutral range by natural procedures in the digester. Two buffering systems ensure this. A too strong acidification is avoided by the carbon dioxide/hydrogen carbonate/carbonate buffer system. During the fermentation, CO_2 is continuously evolved and escapes into air. With falling pH value, more CO_2 is dissolved in the substrate as uncharged molecules. With rising pH value, the dissolved CO_2 forms carbonic acid, which ionizes [13].

3.2.4. Substrate composition and consistency of feed material

In general, all types of biomass can be used as substrates as long as they contain carbohydrates, proteins, fats as main components. Any biodegradable organic materials can be used as an input for biomethanation process. However, for techno-economical reasons, some materials are preferred than the others. Biogas yield and composition of the biogas are greatly affected by the composition of feed materials in respect of carbohydrate, fat and protein contents. Anaerobic digestion of carbohydrates yields 886 L biogas (with methane content of around 50%) per kg of VS destroyed. Similarly, anaerobic digestion of fats yields 1535 L biogas (with methane content of around 70%) per kg of VS and that of proteins yields 587 L biogas (with methane content of around 84%) per kg of VS destroyed [38].

The water content in substrate should be about 90% of the weight of the total contents. With too much water, the rate of biogas production per unit volume of digester decreases, preventing optimum use of the digester. If the water content in substrate is too low, acetic acid is to be accumulated, which inhibit the fermentation process and hence biogas production and also thick scum is to be formed on the surface. The water content differs according to the raw material used for fermentation [47]. In case of fresh cattle dung, it has to be mixed with water on a unit volume basis (i.e. same volume of water for a given volume of dung) before feeding into the digester. However, if the dung is in dry form, the quantity of water has to be increased accordingly to arrive at the desired consistency of the inputs (e.g. ratio could vary from 1:1.25 to even 1:2). The dilution should be kept to maintain the total solids from 7.0% to 10.0%. If the dung is too diluted, the solid particles will settle down into the digester and if it is too thick, the particles impede the flow of gas formed at the lower part of digester. In both the cases, the gas production will be less than optimal.

3.2.5. Organic loading rate

The organic loading rate (OLR) is defined as the amount of volatile solids (VS) or chemical oxygen demand (COD) components fed per day per unit digester volume. Higher organic loading rates can reduce both the digester's size and consequently, the capital cost. However, enough time (retention time) should be permitted for the micro-organisms to break down the organic material and convert it into gas [48]. Methanogens vary considerably with regard to specific carbon requirements and growth response to organic additions [36]. For optimum gas yield through biomethanation process, normally an 8.0–10.0% total solid content in the feed is desirable [49]. A total solid concentration of 15.2% has been reported to yield highest gas production in case of dairy manure. Furthermore, it has also been found that in case of fresh dairy manure, a feedstock having total solids between 13.0% and 15.0% appears most ideal [50].

Thermophilic (55 °C) biomethanation of sorghum and sorghum/cellulose mixture containing over 25% total solids at organic loading rates (OLR) of 18 and 24 g/kg/day has been found to yield steady methane production rates of 5.7 and 7.5 L/kg/day, respectively. At above OLR the efficiency of volatile solids (VS) conversion to biogas were reported as 74.8% and 72.1%, respectively [51]. High total solids anaerobic digestion (25–30% effluent total solids) showed the need to address ammonia toxicity and trace nutrient limitations. Trace nutrient supplementation and control of the feedstock C/N ratio enables a stable operation of digesters at volatile solids (VS) loading rates up to 24 g/kg reactor wet mass per day (gVS/kg/d), with mean methane production rate of 7.5 L/kg/d [52]. The higher the volatile solids fed to the digester, the larger the amount of volatile acids formed in the digester. The higher the amount of volatile acids in the digester will show the higher impact of alkalinity and pH of digester. Therefore, sludge that has a high volatile content should be transferred slowly to an anaerobic digester [34].

Table 6
C/N ratio of some organic wastes [13].

Waste	DM content, %	Organic substance % of DM	C/N
Straw	70	90	90
Waste from saw mill	20–80	95	511
Paper	85–95	75	173
Waste from household	40–60	40	18
Sewage sludge	0.5–5	60	6

3.2.6. C/N ratio

A C/N ratio ranging from 20 to 30 is considered optimum for anaerobic digestion process [38]. A C/N value of at least 25:1 is suggested for optimal gas production [34]. If the C/N ratio is very high, methanogens will rapidly consume the nitrogen for meeting their protein requirements and will no longer react with the left over carbon content of the material. As a result, gas production will be low. On the other hand, if the C/N ratio is very low, nitrogen will be liberated and accumulated in the form of ammonium ion (NH_4). The presence of excess NH_4 will increase the pH of the biodigestate in the digester and thus a pH higher than 8.5 will start showing toxic effect on methanogens population [46].

Animal waste, particularly cattle dung has an average C/N ratio of about 24.0. The plant materials such as cereal straw and sawdust contain a higher percentage of carbon. The human excreta have a C/N ratio as low as 8.0. Materials with high C/N ratio could be mixed with those of low C/N ratio to bring the average ratio of the composite input to a desirable level [49]. Substrates with a too low C/N ratio lead to increase ammonia production and inhibition of methane production. A too high C/N ratio means lack of nitrogen, which presents negative consequences for protein formation and thus the energy and structural material metabolism of the micro-organisms results. A balanced composition is absolutely necessary, e.g. the mixture of rice straw and latrine waste is as usual in China and co-fermentation of elephant dung with human waste in Nepal [13]. Table 6 shows the C/N ratio of some common organic wastes.

3.2.7. Long-chain free fatty acid

Long-chain fatty acids of concern include capric, caprylic, lauric, myristic, and oleic acids. The acids contain carbon chains of

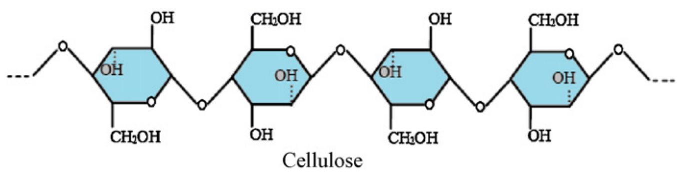


Fig. 3. Schematic of cellulose chain.

8–18 units. Among these lauric acid is the most toxic long-chain fatty acids. Combinations of these acids produce a synergetic effect. Long-chain fatty acids concentrations >500 g/L may cause toxicity in anaerobic digesters [34]. Further, the formation of volatile fatty acids beyond a particular range hinders the methane production [40]. Low concentrations of long-chain fatty acid oleates and stearates have been found to inhibit all the steps of the anaerobic thermophilic digestion process during digestion of cattle manure [53]. In a study, the toxic effect of oleates and stearates is found permanent, as microbial growth does not occurred even when inhibited cultures were diluted to a non-inhibitory concentration. No adaptation to the fatty acid toxicity has been observed by pre-exposing the cultures to non-inhibitory concentrations and the inhibitory response was the same as for cultures not pre-exposed to the fatty acids. Furthermore, oleate is found less inhibitory when added as neutral oil in the form of the glycerol ester [54]. Linseed oil fatty acids and linolenic acid inhibits methane production in the rumen of the animals. For inhibition, a free carboxyl group is necessary [55].

The microbial metabolism processes are dependent on many parameters, so that, for an optimum fermenting process, numerous parameters must be taken into consideration and be controlled. Furthermore, the environmental requirements of the fermentative bacteria, by which the hydrolysis and acidification of the substrates occur, differ from the requirements of the methane-forming microorganisms. Moreover, with all biological processes, the constancy of the living conditions is of great importance. A temperature change or changes in the substrates or the substrate concentration can lead to shutdown gas production. It can last up to 3 or even more weeks, until the ecological system has adapted to the new conditions and starts biogas production again without any intervention from outside. But in the case of any human interference it can take a further 3 weeks [13].

4. Lignocellulosic biomass, properties and its pretreatment

4.1. Lignocellulosic biomass

Plant biomass is mainly composed of cellulose, hemicellulose and lignin along with smaller amounts of pectin, protein, extractives (soluble non-structural materials such as sugars, nitrogenous material, chlorophyll and waxes) and inorganic minerals [56,57]. Thus, lignocellulose is the primary building block of plant cell walls and comprises a large fraction of municipal solid waste, crop residues, woodlot arisings, forest residues and many dedicated energy crops [58].

Cellulose is the main structural constituent in plant cell walls and is found in an organized fibrous structure. The structure of cellulose is shown in Fig. 3. Cellulose in biomass is present in both crystalline and amorphous forms. Crystalline cellulose comprises the major proportion of cellulose, whereas a small percentage of unorganized cellulose chains form amorphous cellulose. Cellulose is more susceptible to enzymatic degradation in its amorphous form. Cellulose is a linear polysaccharide polymer of glucose (β-1,4-glucan) made of cellobiose units. Cellobiose is the repeat unit established through the linkage, and it constitutes cellulose chains. The long-chain cellulose polymers are linked together by hydrogen and van der Waals bonds, so called “elementary and micro-fibrils”. The micro-fibrils are often associated in the form of bundles. These fibrils are attached to each other by hemicelluloses (amorphous polymers of different sugars as well as other polymers such as pectin) and bonded together by lignin [59–62].

Hardwood has greater amounts of cellulose, whereas wheat straw and leaves have more hemicellulose. The dominant sugars in hemicelluloses are mannose in softwoods and xylose in hardwoods and agriculture residues [6,63–65]. The backbone of hemicellulose is either a homo-polymer or a hetero-polymer with short branches linked by β-1,4-glucan bonds and occasionally β-1,3-glucan bonds. In contrast to cellulose, the polymers present in hemicelluloses are easily hydrolysable [66].

Lignin is a very complex large molecule constructed of phenolic monomer units linked in a three-dimensional structure. Three phenyl propionic alcohols exist as monomers of lignin; (i) coniferyl alcohol (guaiacyl propanol), (ii) coumaryl alcohol (p-hydroxyphenyl propanol), and (iii) sinapyl alcohol (syringyl alcohol). Alkyl–aryl, alkyl–alkyl, and aryl–aryl ether bonds links these phenolic monomers together. In general, herbaceous plants such as grasses have the lowest contents of lignin, whereas softwoods have the highest content of lignin. Lignin provide structural support and is almost impermeable and is one of the major drawbacks of using lignocellulosic materials in fermentation, as it makes lignocellulose resistant to chemical and biological degradation [67–69].

4.2. Properties of lignocellulosic biomass

Properties of biomass in term of proximate, ultimate and compositions (carbohydrates, fats, proteins, cellulose and hemicellulose) are of great importance in any biomass-to-energy conversion process. Biomass feedstocks and fuels exhibit a wide range of physical, chemical and agricultural/process engineering properties. Despite their wide range of possible sources, biomass feedstocks are remarkably uniform in many of their fuel properties. Some important properties of major lignocellulosic biomass derived from agriculture, in the vicinity of energy conversion process are as follows.

4.2.1. Proximate properties

In general, air-dried biomass typically contains 15–20% moisture. Remaining fraction of mass is total solids content present in biomass. This solid mass largely contains volatile solids and a little fraction as minerals content (ash). In any energy conversion process, only a part of volatile solids mass undergoes into its conversion. Table 7 presents the proximate properties of major lignocellulosic agricultural based biomass.

4.2.2. Ultimate properties

The major part of biomass is carbon, oxygen and hydrogen. In general, biomass contains about 40–45% mass as oxygen and 35–50% mass as carbon on dry weight basis of biomass. The quantity and quality of product derived in any biomass-to-energy conversion process, is most importantly governed by the ultimate properties of biomass. Furthermore, the knowledge about elemental content in a particular biomass provides help in adjustments for parameters of specific interest in an energy conversion process. Table 8 shows the ultimate properties of some of common lignocellulosic agricultural based biomass.

4.2.3. Compositional properties

The composition of various constituents (cellulose, hemicellulose and lignin) in lignocellulosic biomass varies from one plant species to another. Further, the ratio between various constituents

Table 7
Proximate properties of common agricultural lignocellulosic biomass.

Biomass	Proximate composition			
	Volatile fraction in dry matter, %	Fixed carbon, %	Ash, %	Heating value, MJ/kg dry wt.
Maize stover	75.2, 93.2, 89.7 [73,75,77]	19.3 [73]	7.5, 6.9, 10.3 [70,73,77]	16.2, 16.5 [70,73]
Sugarcane bagasse	70.9 [79]	7.0 [79]	16.0, 14.7, 22.1 [74,76,79]	10.0, 14.3 [25,79]
Sugarcane leaves	77.4 [79]	14.9 [79]	7.7 [79]	17.4 [79]
Wheat straw	79.6, 91.3, 80.6, (88.9) [73,75,79]	16.8, 11.7 [73,79]	8.3, 5.3, 10.5, 7.7, 4.1, (11.1) [70,73,76,79,80]	16.8, 18.4, 17.0, 18.9 [70,73,78,79]
Rice straw	69.3, 70–95, 72.7, (84.0) [73,13,79]	17.3, 11.8 [73,79]	16.2, 14.7, 15.5, (16.0) [73,76,79]	15.3, 14.5 [73,79]
Rice husk	59.5, (75.7) [72]		21.8, 17.1, 22.5, 22.2, (24.3) [71,72,73,76]	12.3, 16.5 [71,73]

Figure in parenthesis ( ) found by the authors.

Table 8
Ultimate properties of common agricultural lignocellulosic biomass.

Biomass	Elemental composition				
	Carbon, %	Hydrogen, %	Oxygen, %	Nitrogen, %	Sulphur, %
Maize straw	45.6 [73]	5.4 [73]	43.4 [73]	0.3 [73]	0.04 [73]
Maize stover	43.7, 35.2 [73,25]	5.6 [73]	43.3 [73]	0.6 [73,77]	0.01 [73]
Sugarcane leaves	39.7 [79]	5.55 [79]	46.8 [79]	0.2 [79]	–
Wheat straw	46.7, 45.5, (45.8) [73,78]	6.3, 5.1, (6.0) [73,78]	41.2, 34.1 [73,78]	0.4, (0.42) [73]	0.1 [73]
Rice straw	41.8, 36.0, (41.0) [73,79]	4.6, 5.3, (5.4) [73,79]	36.6, 43.1 [73,79]	0.7, 0.35-0.70, (0.74) [73,13]	0.08 [73]
Rice husk	37.9, 44.6, 38.2, (36.3) [71,72,73]	4.82, 5.6, 5.6, (4.7) [71,72,73]	34.9, 49.3, 33.7 [71,72,73]	0.43, (0.60) [71]	0.17 [71]

Figure in parenthesis ( ) found by the authors.

Table 9
Cellulose, hemicellulose and lignin contents in common agricultural biomass.

Lignocellulosic biomass	Cellulose, %	Hemicellulose, %	Lignin, %
Corn cobs	45	35	15
Cotton seed hairs	80–95	5–20	0
Grasses	25–40	35–50	10–30
Hardwood stems	40–55	24–40	18–25
Leaves	15–20	80–85	0
Newspaper	40–55	25–40	18–30
Nut shells	25–30	25–30	30–40
Paper	85–99	0	0–15
Softwood stems	45–50	25–35	25–35
Solid cattle manure	1.6–4.7	1.4–3.3	2.7–5.7
Sorted refuse	60	20	20
Waste papers from chemical pulps	60–70	10–20	5–10
Wheat straw	30, 39.2 [80], (35.1)	50, 26.1 [80], (25.6)	15, 21.1 [80], (7.5)
Maize stover	37.5 [77]	30.0 [77]	10.3, 8.4 [75,77]
Rice straw	44.3 [82], (38.9)	33.5 [82], (24.0)	20.4 [82], (5.6)
Rice husk	34.4 [72], (38.3)	29.3 [72], (17.4)	19.2 [72], (18.3)
Sugarcane bagasse	45.0 [81]	20.0 [81]	30.0 [81]

Figure in parenthesis ( ) found by the authors.

within a single plant varies with age, stage of growth and with other conditions [67]. Table 9 presents in general compositions of cellulose, hemicellulose and lignin contents in some of the common agricultural residues and wastes [6,56].

4.3. Pretreatment processes of lignocellulosic biomass

The presence of lignin in lignocellulosic biomass leads to a protective barrier to the biomass and provide resistance to

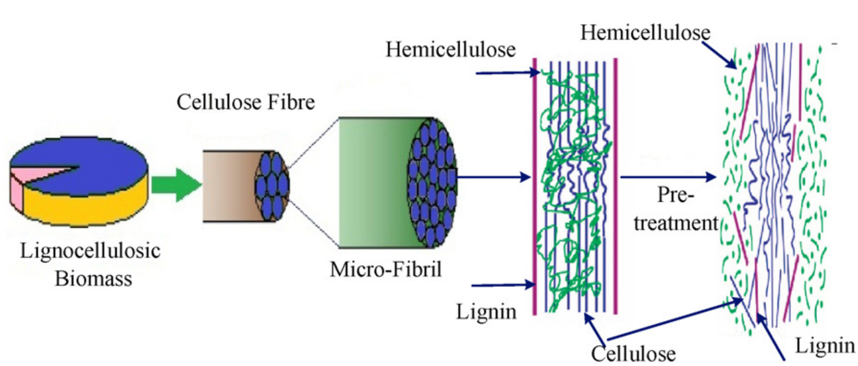


Fig. 4. Schematic of role of pretreatment of lignocellulosic biomass.

Table 10
Pretreatment methods for lignocellulosic biomass [88].

Sl. No.	Method/Process	Types	Possible changes in biomass and notable remarks
(A) Mechanical or physical			
1	Grinding/milling		
		Hammer milling Ball milling Two-roll milling Colloid milling Vibro milling (Electroporation)	Due to size reduction accessible surface area and pore size increases. Thus, decreases cellulose crystallinity Lignin cannot be removed Most of the methods require high energy No chemical requirement
2	Irradiation		
		Gamma ray Electron beam Microwave	Leads to cleavage of β-1,4-glucan bonds and gives a larger surface area and a lower crystallinity
3	Others		The cellulose component of the lignocellulose materials can be degraded to fragile fibres and low molecular weight oligosaccharides and cellobiose. This method is too expensive
		Hydrothermal High pressure steaming Expansion Extrusion	
		Pyrolysis	Cellulose rapidly decomposes to gaseous products and residual char when biomass is treated at temperatures greater than 300 °C
(B) Chemical and physico-chemical			
1	Alkali		
		Sodium hydroxide	Efficacy order of alkali (NaOH > KOH > $Mg(OH)_2$ and $Ca(OH)_2$)
		Potassium hydroxide Calcium hydroxide Magnesium hydroxide Ammonia Ammonium sulphite	Increase in accessible area. Partial or nearly complete delignification Decrease is cellulose crystallinity Decrease in degree of polymerization Partial or complete hydrolysis of hemicellulose
2	Acid		
		Sulphuric acid Hydrochloric acid Phosphoric acid	
3	Gas		
		Chlorine dioxide Nitrogen dioxide Sulphur dioxide	These methods are the most effective and promising processes for industrial applications
4	Explosion		
		Steam explosion Ammonia fibre explosion CO_2 explosion SO_2 explosion	These methods usually have rapid treatment rate and need harsh conditions
5	Oxidizing agents		
		Hydrogen peroxide Wet oxidation Ozonolysis	
6	Solvent extraction of lignin		
		Ethanol–water Benzene–water Butanol–water Ethylene glycol Swelling agents	
(C) Biological			
1	Fungi and actinomycetes		
			Delignification and reduction in degree of polymerization of cellulose and partial hydrolysis of hemicellulose. Low energy requirement, no chemical requirement and mild environmental conditions are the main advantages. However, the treatment rate is very low in most of the biological pretreatment processes

any chemical and biological degradation that prevents plant cell destruction by fungi, bacteria and enzymes. For the conversion of biomass-to-fuel, the cellulose and hemicellulose must be broken down into their corresponding monomers sugars, so that micro-organisms can utilize them in the energy conversion process through biological route. Thus, the aim of pretreatment is to break the impermeable/resistant layer of lignin, so that the cellulose and hemicellulose present in the biomass is hydrolysed by the micro-organisms and converted into simple sugars. Fig. 4 presents the schematic role of pretreatment of lignocellulosic biomass.

Numerous articles on pretreatment of lignocellulosic biomass have been published recently in literature by various researchers [6,83–90] for production of biofuels/bio-chemicals. Pretreatment

Table 11
Estimated average biochemical methane potential of some lignocellulosic agricultural crop biomass.

Sl. no.	Biomass	Average methane production potential	
		m^3/kg VS_a	m^3/kg TS_a
1	Maize crop waste	0.338	0.290
2	Wheat straw	0.290	0.243
3	Rice straw	0.302	0.232
4	Sugarcane crop waste	0.278	0.206

offers increase in accessible surface area and porosity, decrease in crystallinity of cellulose and hemicellulose and degree of polymerization. These pretreatment processes are broadly classified under three categories; (i) mechanical or physical, (ii) chemical and physico-chemical, and (iii) biological. Table 10 shows various processes of pretreatment under each category. The selection of particular pretreatment method is one of the important factors that depend upon the type and various constituents present in biomass. Furthermore, the pretreatment must meet the following requirements; (i) it must improve the formation of sugars or the ability to subsequently form sugars by hydrolysis, (ii) it must avoid the degradation or loss of carbohydrate, (iii) it must avoid the formation of by-products that are inhibitory to the subsequent hydrolysis and fermentation processes, and (iv) it should be cost-effective.

The pretreatment of lignocellulosic biomass offers higher biodegradation rate and overall main product yield in any biological energy conversion processes. He et al. [91] reported that the solid state NaOH pretreatment of rice straw at 4%, 6%, 8% and 10% (dry weight basis NaOH) increased the biogas production yield by 3.2–28.6%, 27.3–64.5%, 30.6–57.1% and 15.2–58.1% than that of untreated, respectively for organic loading rates of 35, 50, 65 and 80 g/L in the fermentation digester. They also reported that the highest biogas production occurred at organic loading rate of 50 g/L [91]. Pang et al. [92] reported that 6% NaOH pretreated corn stover at 65 g/L organic loading rate had increased 48.5% more biogas yield and 71.0% more bio-energy as compared to the untreated corn stover substrate [92]. Alkali pretreatment of lignocellulosic biomass has been found to cause swelling, leading to increase in internal surface area, decrease in degree of polymerization and crystallinity, separation of structural linkages between lignin and carbohydrates (cellulose and hemicellulose), and disruption of lignin structure. Further, alkaline pretreatment reduces the degree of inhibition during fermentation and provides a lower production cost compared with other pretreatment methods [87,93,94]. Reaction temperature and residence time are two very important parameters for disruption of lignocellulosic structure. Reaction temperature of 190 °C and residence time of 5–10 min is high enough to destroy hemicellulose and crystalline structure of cellulose. Lesser reaction residence time can save energy in contrast to higher residence time [95].

Hydrothermal pretreatment of lignocellulosic biomass for enhanced bio-ethanol and biogas production is gaining high importance in the 21st century. Water under high pressure and

Table 12
Ethanol production yields from some renewable lignocellulosic feedstocks [107,108].

Sl. no.	Biomass feedstocks	Ethanol yield, L/tonne of dry biomass
1	Sugarcane bagasses	424
2	Corn stover	428
3	Rice straw	416
4	Wheat straw	386
5	Forest residue	310
6	Saw dust	382

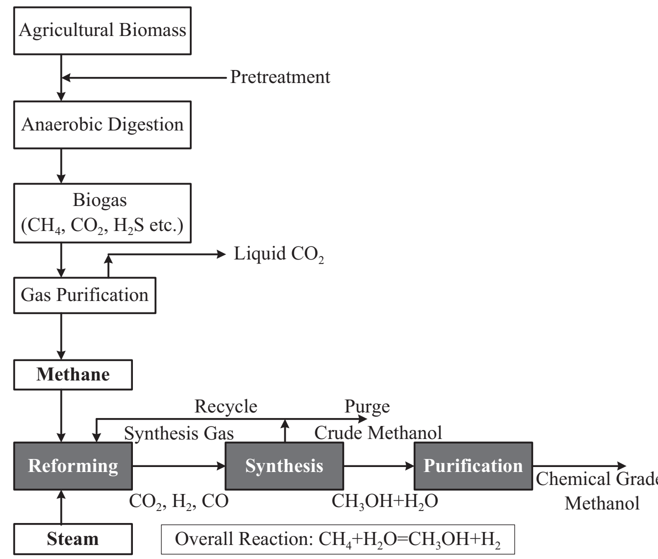


Fig. 5. The methane-to-methanol production process from landfill gas/biogas system.

temperature can penetrate into the biomass, hydrate cellulose, and remove hemicellulose and part of lignin. The major advantages are no addition of chemicals and no requirement of corrosion-resistant materials for hydrolysis reactors in this process. The feedstock size reduction is a highly energy demanding operation on a commercial scale. However, there could be no need for size reduction in hydrothermal pretreatment process and requires much lower need of chemicals for neutralization of the produced hydrolyzate and produces lower amounts of neutralization residues compared to many processes. Hydrothermal pretreatment enhances the accessible and susceptible surface area of the cellulose and make it more accessible to hydrolytic enzymes [88,96]. The increase in operating temperature of hydrothermal pretreatment causes higher saturated water vapour pressure, which results into faster hydrolysis of volatile matter contents. However, it increases the energy requirement in the pretreatment process. Furthermore, higher residence time causes pyrolysis resulting into charring of biomass along with higher energy requirement. Further again, hydrothermal pretreatment decreases the pH of biomass slurry, which might be caused by hydrothermal oxidation of sulphur and phosphorus present in the biomass, which results into production of inorganic acids.

Furthermore, an appropriate range of alkalinity is of paramount importance for methane-forming bacteria during the methane fermentation process. Therefore, addition of certain alkaline compound is an essential requirement in the substrates prepared using hydrothermal pretreatment method. Addition of appropriate amount of alkali helps to ensure adequate alkalinity to neutralize the acids within the digester as most anaerobic bacteria perform well within a pH range of 6.8–7.2. Further, the increased cations concentrations more than 1500 mg/L begin to exhibit significant toxicity [34]. Therefore, care should be taken while deciding the addition level of particular alkali into the substrate, so that it should not be beyond the inhibitory level for the process. Hydrothermal pretreatment followed by addition of appropriate amount of NaOH is a potentially effective and is a best method for pretreatment of lignocellulosic biomass (rice husk and rice straw) to enhance biogas and methane production yields. Rice straw hydrothermal pretreated substrate (200 °C temperature and 10 min residence time) followed by addition of 5% NaOH has resulted into a biogas and methane production yields of 315.9 L/kg VS_a and 132.7 L/kg VS_a, respectively. The same has resulted into an increase of 225.6%

Table 13
Estimated energetic of methane and ethanol production potentials.

Sl. no.	Biomass	Methane production		Ethanol production	
		Yield, kg/tonne	Energy, MJ	Yield, kg/tonne	Energy, MJ
1	Maize crop waste	208.80	10440.00	338.12	9061.616
2	Wheat straw	174.96	8748.00	304.94	8172.392
3	Rice straw	167.04	8352.00	328.64	8807.552
4	Sugarcane crop waste	148.32	7416.00	334.96	8976.928

Methane properties: relative density = 0.72, higher heating value = 50.0 MJ/kg [7], ethanol properties: relative density = 0.79, higher heating value = 26.8 MJ/kg [109].

in biogas production and 222.0% in methane production relative to untreated rice straw substrate [97].

5. Methane generation potential of lignocellulosic agricultural biomass

The biochemical methane potential (BMP) yield of various kinds of agricultural lignocellulosic biomass wastes has been determined by various researchers and is available in literature [13,29,75,80,98–106]. Based on their experimental findings, the methane production potential of maize, wheat, rice and sugarcane crops biomass are presented herewith.

Weiland [98] has reported biochemical methane potential of maize stover as 0.410 m^3/kg volatile solids added. Deublein and Steinhauser [13] reported that the biogas production from maize straw yields 0.40–1.0 m^3/kg of organic total solids with a methane content of about 55%. Tong et al. [75] and Richards et al. [99] reported a value of methane production potential of maize stover as 0.360 and 0.300–0.326 m^3/kg volatile solids added, respectively. Lane [100] reported the methane production potential value of 0.267 m^3/kg volatile solids from maize cobs.

Weiland [98] reported the methane production yield of wheat straw biomass as 0.390 m^3/kg organic dry matter fed to the anaerobic digester. Sharma et al. [101] and Moller et al. [102] reported the methane production potential of wheat straw as 0.162–0.249 and 0.145–0.161 m^3/kg volatile solids, respectively. Hashimoto [103] reported the methane production potential of untreated and sodium hydroxide treated wheat straw as 0.304 and 0.367–0.383 m^3/kg of volatile solids added, respectively. Gunaseelan [104] reported a methane production potential range from 0.190 to 0.327 m^3/kg volatile solids added for wheat straw. Tong et al. [75] reported a value of biochemical methane potential of 0.302 m^3/kg of volatile solids fed to digester. Kaparaju et al. [80] reported, methane production yield of wheat straw effluent of bio-ethanol and bio-hydrogen productions, as 0.324 and 0.381 m^3/kg volatile solids, respectively.

The biochemical methane potential of rice straw in batch assay has been reported as 0.241–0.367 m^3/kg of volatile solids added by Sharma et al. [101] for straw sizes of 30–1 mm. Deublein and Steinhauser [13] reported the biogas production yield of rice straw ranges from 0.550 to 0.620 m^3/kg of organic total solids fed to the anaerobic digester, with a methane content of about 55% in produced biogas. Lei et al. [105] reported the biogas and biochemical methane potential yield of rice straw vary from 0.330 to 0.350 and from 0.270 to 0.290 m^3/kg of volatile solids, respectively. Deublein and Steinhauser [13] has reported that the biogas production yield from anaerobic digestion of most of the straw from cereal crops varies from 0.200 to 0.500 m^3/kg of organic total solids fed to the anaerobic digester.

The biochemical methane potential of sugarcane biomass has been reported to vary from 0.266 to 0.314 m^3/kg volatile solids and from 0.230 to 0.300 m^3/kg volatile solids, respectively by Deren and Snyder [29] and Chynoweth et al. [106]. Table 11 shows the average approximate methane production potential yields of the major lignocellulosic agricultural biomass, estimated by using the values obtained by various researchers.

6. Analysis of methane and bio-ethanol productions

An energetic comparison of methane and bio-ethanol productions from lignocellulosic agricultural biomass has been estimated using baseline reference data of methane and bio-ethanol production yields and their properties. Bio-ethanol production yield of some of major lignocellulosic agricultural/forestry biomass is presented in Table 12 [107,108]. Methane and ethanol production yields of maize, wheat, rice and sugarcane crops waste biomass

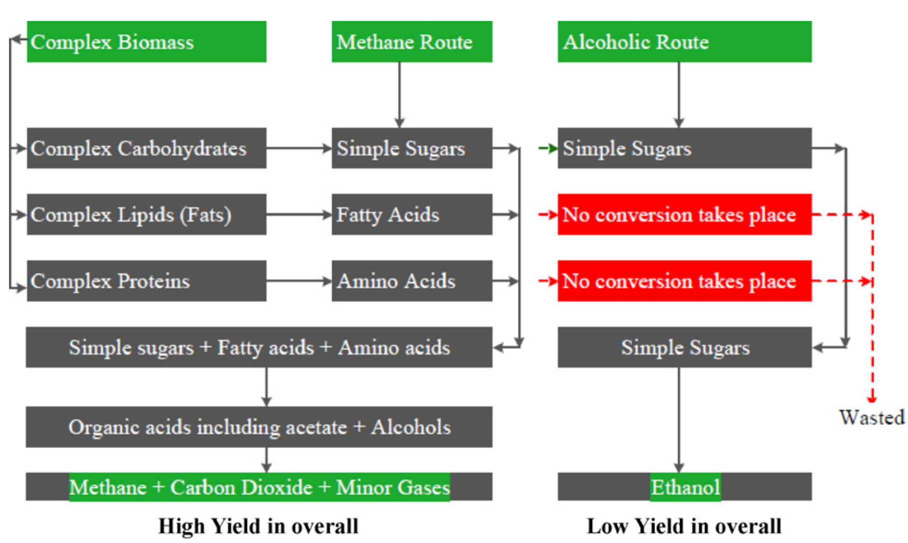


Fig. 6. Schematic representation of overall part of biomass content utilization in the processes of methane fermentation and alcoholic fermentation.

per tonne of dry matter of biomass has been determined using Tables 11–12. Furthermore, the energy value of output products i.e. methane and bio-ethanol on unit tonne basis is shown in Table 13.

The analysis of table reveals that the methane/bio-ethanol energy ratio for maize, wheat, rice and sugarcane based lignocellulosic biomass is to be about 1.15, 1.07, 0.95 and 0.83, respectively. This output energy ratio of methane/bio-ethanol may further increases, since the ethanol production from lignocellulosic biomass requires more input energy in various involved unit operations rather than the methane production through anaerobic digestion. In general, about 9–10 MJ input energy per litre output of bio-ethanol is consumed in most of the common bio-refinery process of bio-ethanol production from lignocellulosic biomass [110]. Advanced technologies of bio-refinery of bio-ethanol production from cellulosic biomass involve two-step pretreatment (dilute acid pre-hydrolysis and enzymatic saccharification), which consume a substantial amount of energy. Generally, an energy input of 0.633 MJ/kg of bio-ethanol is required in advanced bio-refinery process of bio-ethanol production from corn stover [110].

Bio-ethanol production is only a choice to produce liquid fuel that can be directly blended into gasoline and diesel fuels. It is technically possible to produce renewable methanol liquid fuel from the methane. Fig. 5 shows the complete process of methane-to-methanol production from the landfill gas/biogas system. Landfill gas/biogas to renewable methanol is technically the most challenging issue, since contaminants removal to parts per billion is required to manufacture methanol, and that is only possible by the CO_2 Wash^{TM} technology. The CO_2 Wash^{TM} can remove the contaminants from landfill gas/biogas using liquid carbon dioxide condensed directly from the landfill gas/biogas. A stream of contaminant-free methane and carbon dioxide is produced, along with a condensed stream of contaminants in carbon dioxide. This intermediate stream of clean methane and carbon dioxide can be used as fuel gas or as feedstock to make renewable methanol [111].

Two very important parameters in any biomass-to-energy conversion process are; (i) overall contents of biomass utilization in the process, and (ii) overall input energy required in the process. Fig. 6 presents the schematic of the overall contents of the biomass utilization in anaerobic digestion as well as in alcoholic fermentation routes of the biological energy conversion process. It is clearly evident that the almost major part of the biomass contents (carbohydrates, fats and proteins) in anaerobic digestion process, is converted into simple derivatives and finally into methane and carbon dioxide with help of the different types of anaerobic and methanogenic bacteria. However, in case of alcoholic fermentation process, only carbohydrates is converted into simple sugars and finally into ethanol. Thus, the bio-ethanol recovery yield is lower than the methane yield. Moreover, lignocellulosic agricultural biomass is primarily composed of cellulose, hemicellulose and lignin. However, it also contains about 1–2% fat and 3–4% crude protein [112]. The fat and protein content part of biomass remains unutilized in alcoholic fermentation process. Thus, methane fermentation route is always better in term of overall contents of biomass utilization in the process.

The overall analysis, considering various involved parameters in anaerobic digestion and alcoholic fermentation may results into "methane production through anaerobic digestion process is always a better option than bio-ethanol production" more economical and environmentally beneficial way of utilization of lignocellulosic agricultural crop wastes biomass.

7. Conclusions

This paper has discussed the importance and potential application of major lignocellulosic agricultural crops (maize, wheat, rice and sugarcane) produced waste biomass, in order to produce and utilize renewable biogas energy via methane fermentation route. Huge amount of agricultural biomass is burnt annually in field/open environment that releases harmful gases and is not a way of sustainable development of society. The prime concern of "second generation of biofuel production" is to produce renewable fuels/chemicals from agricultural wastes biomass in order to meet the goals of sustainable and ecological development of earth planet. Lignocellulosic agricultural crops waste/biomass has huge unutilized potential in order to meet energy/fuel demand. Furthermore, in order to generate renewable fuel/energy in a sustainable way, the energy efficient fermentation of lignocellulosic agricultural biomass seems to be a best idea for developed as well as developing countries. It would be economic and would contribute to environmental protection. Moreover, methane fermentation technology is a most efficient way of biomass utilization for energy generation in term of energy output/input ratio among all the biological and thermo-chemical routes of energy conversion processes. Only a little harmful or unpleasant material (volatile organic compounds) would releases during methane fermentation process.

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